PERKIN 1

Enantiomerically pure cyclopropylboronic esters: auxiliary- *versus* substrate-control

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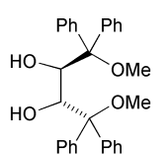
Stable, enantiomerically pure cyclopropylboronic esters are synthesized from alkynes by a hydroboration–cyclopropanation sequence. The direct hydroboration—utilizing 1,3,2-dioxaborolane **4**—is most convenient, however, with more functionalized side-chains it failed to give the desired intermediates. Using the more reactive dicyclohexylborane, followed by oxidation and transesterification, is a good alternative one-pot conversion. Cyclopropanations were performed either following a Simmons–Smith protocol or with diazomethane–palladium(II) acetate. The influence on the diastereoselectivity of the auxiliary **1** is compared with the influence of an additional stereogenic center in the side-chain.

Introduction

Cyclopropylboronic esters have attracted considerable interest as general building blocks for cyclopropanes. Since the first reports of their successful synthesis,[1–4] various groups proved the versatility of this approach, *e.g.* by demonstrating that the Suzuki coupling of these boron intermediates is possible.[5–15] Furthermore, after the first diastereoselective cylopropanations by Imai *et al.*,[16] new auxiliaries, *e.g.* **1**, were developed that



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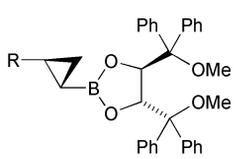
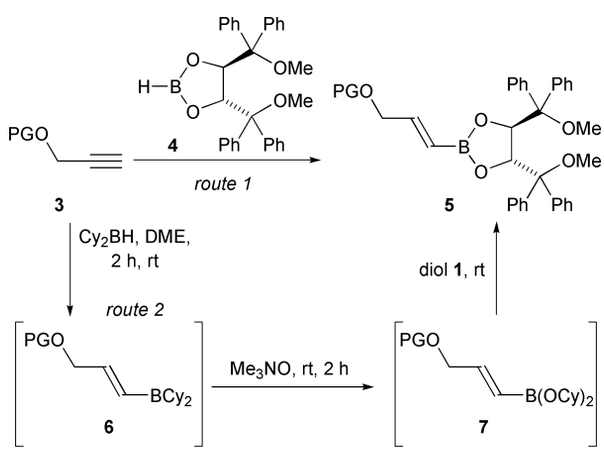


2

would increase the stability of the cyclopropylboronic esters **2** thus allowing chromatographic separations of the diastereoisomers giving enantiomerically pure *cis*-[17] or *trans*-disubstituted[11,18,19] cyclopropanes. A major set-back was the lack of substrate generality; all model reactions with cyclopropylboronic esters were usually performed with substrates with no additional functional group or stereogenic centers in the side-chain. We now present a detailed account closing this gap.

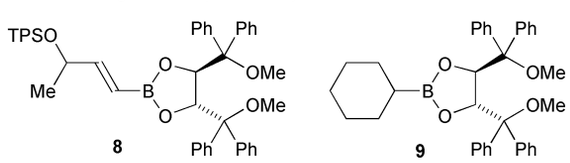
Results and discussion

We chose different protected propargyl alcohols **3** as model compounds for this study. Direct hydroboration of alkynes with 1,3,2-dioxaborolane **4** is usually the method of choice to form alkenylboronic esters, however, with functionalized alkynes **3** this changed. Whereas silyl protecting groups (compounds **3a/b**) did not interfere and the synthesis of the corresponding alkenylboronic esters **5a/b** was straightforward (route 1), ethers, acetals and esters (compounds **3c**–**e**) would not allow the convenient formation of olefins **5c**–**e**. In order to achieve the desired transformations we chose a three-step, one-pot sequence using the more reactive dicyclohexylborane (route 2), a protocol that was first employed for various diols by Vaultier *et al.*[20] and Hoffmann and Dresely.[21] The hydroboration to vinylboranes **6** was followed by the selective oxidation with anhydrous trimethylamine *N*-oxide[22–24] and transesterification of the intermediates **7** with diol **1** to the alkenylboronic esters **5c**–**e** (Scheme 1). Although branched alkynes could also be



Entry	PG	Yield from Route 1 [%]	Yield from Route 2 [%]
a	TBS	91 [ref. 11]	n.p.
b	TPS	60[a]	n.p.
c	Bn	(30) [ref. 11]	47
d	MOM	- [ref. 11]	38
e	Bz	- [ref. 11]	60

TBS = Bu^tMe_2Si; TPS = Bu^tPh_2Si; Bn = benzyl; Bz = benzoyl; MOM = methoxymethyl; PG = protecting group; n.p. = not performed; [a]minor amounts of a regioisomer (Scheme 2) could not be removed.



Scheme 1 Synthesis of alkenylboronic esters **5**.

successfully transformed, the diastereomeric products **8** could not be obtained in pure form. We succeeded in separating neither the common side-product **9**—which was presumably

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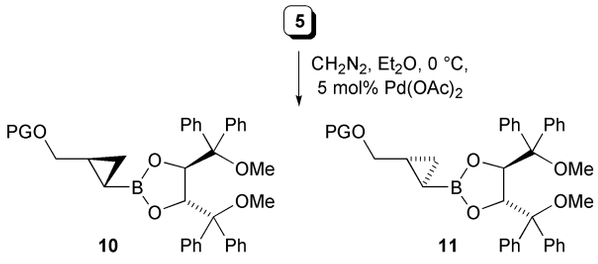
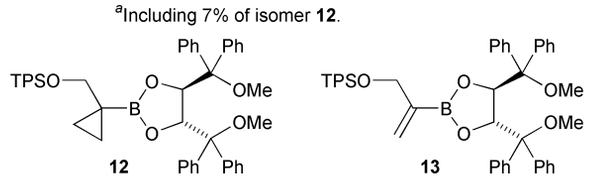
formed after incomplete consumption of dicyclohexylborane in the first step—nor the diastereoisomers.

The cyclopropanation was performed with diazomethane–palladium(II) acetate using our optimized reaction conditions (Scheme 2).[11] The yields were usually high (88–98%) and the



Entry	PG	Yield of **10+11** [%]	dr **10:11**
a	TBS	90 [ref. 11]	70:30
b	TPS	90[a]	66:34
c	Bn	88	80:20
d	MOM	98	86:14
e	Bz	96	83:17

[a]Including 7% of isomer **12**.



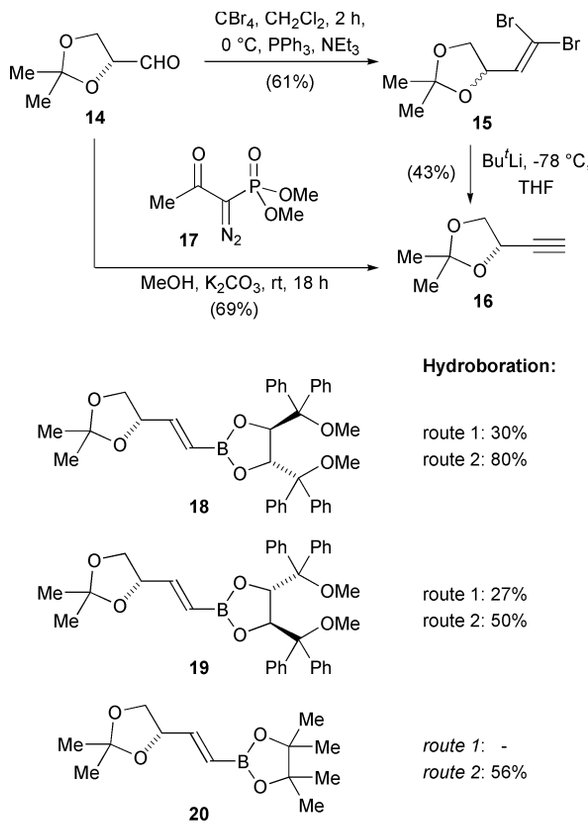
Scheme 2 Synthesis of cyclopropanes **10** and **11**.

diastereomeric ratios moderate to good (dr 66:34 to 86:14). When starting with alkenylboronic ester **5b**, we were surprised to isolate not only the desired separated diastereoisomers **10b/11b**, but also another unprecedented isomer **12**. This is explained by the presence of an additional compound in the starting material whose structure could now be assigned to regioisomer **13**.

Next, we addressed the question of the influence of an additional stereogenic center in the side-chain. Starting from 2,3-*O*-isopropylidene-D-glyceraldehyde **14**,[25–27] we first followed a modified[28] Corey–Fuchs[29] sequence *via* the dibromoalkene **15** to alkyne **16** (Scheme 3). We found that the yields were poor, but—even worse—we observed (not surprisingly) partial racemization during the first step.[28] This was proved by measuring the optical rotation of all intermediates, and later by the formation of diastereomeric hydroboration products. The most convenient synthesis of alkyne **16** utilizes the Bestmann–Ohira reagent **17**.[30–35] In a single step aldehyde **14** was converted (69%) without racemization of the starting material.

The following hydroboration was performed by both routes outlined in Scheme 1. Again, we found that the three-step, one-pot sequence—introducing diol **1**, *ent*-**1** and pinacol in the last step—was superior to the direct hydroboration, furnishing alkenylboronic esters **18**–**20** in 50–80% yield. The only side-product isolated was the cyclohexylboronic ester **9** (and *ent*-**9**, when diol *ent*-**1** was used; the corresponding pinacol derivative was also detected, but could not be obtained).

All three alkenylboronic esters **18**–**20** were cyclopropanated using our standard conditions (diazomethane–palladium(II) acetate; method A) and the Simmons–Smith reaction,[36–38] in particular the Furukawa protocol (method B).[39,40] Generally speaking, method A led to higher yields (A: 88–95%; B: 58–72%), but it was less selective as compared to method B (Fig. 1). The influence of the additional stereogenic center in the side-chain on the diastereomeric ratio depends on the method used. Simplifying, the cyclopropanation with diazomethane can be regarded as predominantly auxiliary-controlled, whereas the Simmons–Smith reactions are substrate-controlled. It is



Scheme 3 Synthesis and hydroboration of alkyne **16**.

Olefin	Method	Product	Yield [%]	dr
18	A	**21+22**	93	83:17
18	B	**21+22**	58	11:89
19	A	**23+24**	95	50:50
19	B	**23+24**	72	94:6
20	A	**25+26**	(88)	60:40
20	B	**25+26**	(60)	95:5

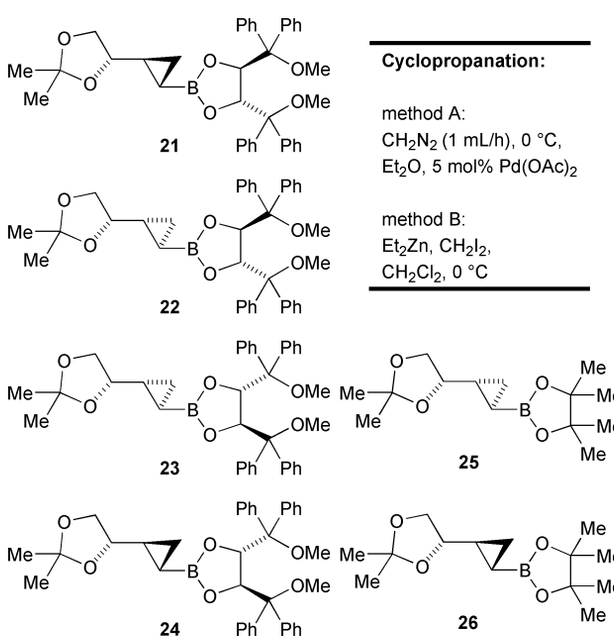
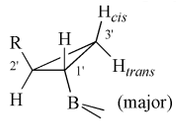
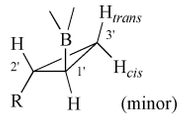


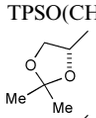
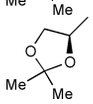
Fig. 1 Diastereoselective cyclopropanation of alkenylboronic esters **18**–**20**.

important to note that just by changing the reaction conditions for the transformation of olefin **18**, the ratio of cyclopropylboronic esters **21**:**22** could be reversed. Unfortunately, only the

Table 1 Characteristic NMR data of cyclopropylboronic esters; assignment of their absolute configuration





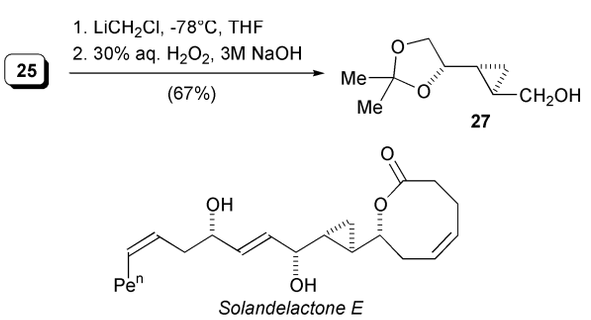
R	Compound	2′-H	3′-H_{trans}	C-2′	C-3′	Compound	2′-H	3′-H_{trans}	C-2′	C-3′
$TBSOCH_2$	**10a**[11]	0.65	0.43	20.0	9.6	**11a**[11]	0.99	0.08	20.0	9.8
$TPSOCH_2$	**10b**	0.59	0.33	20.2	9.5	**11b**	0.91	−0.01	20.4	10.1
$BnOCH_2$	**10c**	0.64	0.46	17.4	10.1	**11c**	1.00	0.10	17.7	10.1
$MOMOCH_2$	**10d**	0.66	0.50	17.3	10.0	**11d**	1.01	0.14	17.5	10.0
$BzOCH_2$	**10e**	0.68	0.38	16.4	9.9	**11e**	1.00	0.00	16.7	10.0
Bu^n	**10f**[11]	0.26	0.31	18.3	11.7	**11f**[11]	0.57	−0.06	18.6	11.8
n-Pentyl	**10g**[11]	0.26	0.31	18.4	11.7	**11g**[11]	0.57	−0.06	18.6	11.8
Bu^t	**10h**[11]	0.49	0.20	29.4	7.7	**11h**[11]	0.59	−0.26	29.6	7.9
Ph	**10i**[11]	1.36	0.80	22.1	15.5	**11i**[11]	1.74	0.43	22.7	15.1
$HOCH_2$	**10j**[11]	0.64	0.41	20.4	9.4	**11j**[11]	1.00	0.06	20.9	9.6
$TPSO(CH_2)_3$	**10k**[11]	0.25	0.30	18.0	11.5	**11k**[11]	0.58	−0.05	nd[c]	nd
	**21**	0.55	0.35	19.4	7.6	**22**	0.81	0.11	19.7	9.8
	[a]	0.59	0.48	19.5	9.4	[b]	0.79	−0.04	19.9	7.7

[a] Obtained when the hydroboration–cyclopropanation sequence was performed with partially racemized alkyne **16**; the NMR data are identical with the enantiomeric compound **23**. [b] Obtained when the hydroboration–cyclopropanation sequence was performed with partially racemized alkyne **16**; the NMR data are identical with the enantiomeric compound **24**. [c] nd: not determined.

boronic esters **21**–**24** could be separated into the pure diastereoisomers; we were not able to perform this purification with the pinacol-derived compounds **25/26**.

Up to this point we took the assignment of the absolute configurations for granted. In fact, we have already shown that the ^1H NMR shifts for the 2′-H and the 3′-H_{trans} protons of the cyclopropane moiety are diagnostic.[11] As can be seen from Table 1, all new compounds match perfectly in the series. Apart from these characteristic relative high-field shifts of the 2′-H protons and down-field shifts of the 3′-H_{trans} protons (major relative to minor diastereoisomer), the ^{13}C NMR data are also to a certain extent diagnostic. In particular the C-2′ carbons are all shifted to high fields for the major diastereomers; the data for the C-3′ carbons are less reliable and depend on the nature of the side-chain.

For the diastereoisomers **25** (**26**) we had no precedent to establish the absolute configuration *via* the NMR data. Consequently, we performed a chemical correlation. Transformation of boronic ester **25** by a Matteson homologation[41] yielded the primary alcohol **27**, a product whose enantiomer had



Scheme 4 Determination of the absolute configuration of cyclopropylboronic ester **25**.

previously been reported (Scheme 4).[42] No sequential insertion was observed.[43] The cyclopropane derivative **27** itself was proposed to be a key intermediate for the construction of the right hand fragment of solandelactones, *e.g.* solandelactone E.[44,45]

Conclusion

A sequence for the synthesis of a variety of enantiomerically pure cyclopropylboronic esters **10/11** has been established. The flexible approach allowed the isolation not only of products with more functionalized side-chains, but also enabled the investigation of the influence of additional stereogenic centers in the substrate (**18**–**20**) on the diastereoselectivity. The investigation proved that depending on the cyclopropanation condition the reaction was either predominantly substrate-controlled (Simmons–Smith protocol) or auxiliary-controlled (diazomethane–palladium(II) acetate). The absolute configurations of all products were confirmed by means of characteristic NMR data of the boronic esters or by chemical correlation. As a consequence, an advanced intermediate **27** for the total synthesis of solandelactones was isolated.

Experimental

All reagents were used as purchased from commercial suppliers without further purification. The alkynes **3** were synthesized using standard procedures and the spectroscopic data were in agreement with published data.[46–49] Aldehyde **14**[25–27] and the Bestmann–Ohira reagent **17**[30–35] were prepared according to the references given. The reactions were carried out using standard Schlenk techniques under a dry nitrogen atmosphere. Glassware was oven-dried at 150 °C overnight. Solvents were dried and purified by conventional methods prior to use; diethyl ether, 1,2-dimethoxyethane, and tetrahydrofuran were freshly distilled from sodium–benzophenone. Petroleum ether refers to the fraction with a boiling point between 40 and 60 °C. **Caution**: The generation and handling of diazomethane requires special precautions.[50–52] Flash-column chromatography: Merck silica gel 60, 0.040–0.063 mm (230–400 mesh). TLC: Pre-coated sheets, Alugram SIL G/UV_{254} Macherey–Nagel; detection by UV extinction or by cerium molybdenum solution [phosphomolybdic acid (25 g), $Ce(SO_4)_2{\cdot}H_2O$ (10 g), conc. H_2SO_4 (60 mL), H_2O (940 mL)]. Preparative MPLC: Gilson (Spectrochrom), with a packed column (49 × 500 mm), LiChroprep, Si60 (15–25 μm), and UV detector (259 nm). ^1H and ^{13}C NMR spectra were recorded—at room temperature in $CDCl_3$ unless otherwise

indicated—on a Bruker A 500. Chemical shifts δ are given in ppm relative to resonances of the solvent (^{1}H: $CHCl_3$, 7.25 ppm; ^{13}C: $CDCl_3$, 77.0 ppm), coupling constants J are given in hertz; in spectra of higher order δ and J values were not corrected. ^{13}C signals were assigned by means of C–H- and H–H-COSY spectra. Microanalysis: performed at the Institut für Organische Chemie, Stuttgart. Melting points (Büchi 510) were not corrected. Specific rotations were measured at 21 °C unless otherwise stated; $[a]_D$ values are given in 10^{-1} deg cm^2 g^{-1}.

Preparation of alkenylboronic esters

General procedure A (route 1). Diol **1** (1 equiv.) was carefully dried at 50 °C under reduced pressure for 1 h. Under an atmosphere of nitrogen, dichloromethane (1 mL per 2 mmol diol **1**) was added and the solution cooled to 0 °C. $BH_3{\cdot}SMe_2$ complex (1.2 equiv. of a 12 M solution in dimethyl sulfide) was added dropwise with vigorous stirring, followed by refluxing the mixture for 4 h. The solvent was removed, the reagent cooled to 0 °C, and the alkyne (1.5 equiv.) slowly added. The flask was closed with a septum, slowly heated to 120 °C and kept at this temperature for 12 h. After cooling to room temperature standard work-up followed,[11,18,19] giving alkenylboronic esters. The yields are given in Scheme 1; the reaction was typically performed on a 1–2 mmol scale.

General procedure B (route 2).[21] Under an atmosphere of dry nitrogen $BH_3{\cdot}SMe_2$ complex (1.0 equiv. of a 12 M solution in dimethyl sulfide) in 1,2-dimethoxyethane (1 mL per mmol borane) was cooled to 0 °C. After addition of cyclohexene (2.0 equiv.) and removal of the cooling bath, a colourless precipitate formed. After 2 h the reaction mixture was cooled to 0 °C, followed by the addition of the appropriate alkyne (1.3–1.5 equiv.). The mixture was stirred at this temperature for 15 min, then allowed to warm to room temperature. Stirring was continued for 2–4 h, during which time a clear solution formed. Trimethylamine *N*-oxide[22–24] (2 equiv.) was carefully added at a rate keeping the reaction under gentle reflux. After 2 h at room temperature the diol **1** (1 equiv.) was added. The reaction mixture was stirred until complete consumption (as judged by TLC) of diol **1** was indicated. The solvent was removed under reduced pressure and the crude product subjected to flash-column chromatography on silica gel, eluting with petroleum ether–diethyl ether (12:1 to 4:1). The yields are given in Scheme 1; the reaction was typically performed on a 1–40 mmol scale.

(4*R*,5*R*)-2-[(*E*)-2-(*tert*-Butyldiphenylsiloxymethyl)ethenyl]-4,5-bis[methoxydiphenylmethyl]-1,3,2-dioxaborolane (5b). Yield 60% (route 1), white foam; softening range = 69–75 °C; $[a]_D$ −30.5 (*c* 0.40 in $CHCl_3$) (Found: C, 77.38; H, 6.89. $C_{49}H_{51}BO_5Si$ requires C, 77.56; H, 6.77%); IR (film)/cm^{-1} 2932, 2857, 2360, 1341 and 1077; NMR δ_H (500 MHz; $CDCl_3$) 0.93 (9 H, s, Me_3C), 2.92 (6 H, s, O*Me*), 4.02 (2 H, dd, *J* 3.5 and 1.8, 1″-H), 5.28 (2 H, s, 4-H and 5-H), 5.43 (1 H, dt, *J* 18.0 and 1.8, 1′-H), 6.16 (1 H, dt, *J* 18.0 and 3.5, 2′-H), 7.17–7.53 (30 H, m, Ar*H*); δ_C (125 MHz; $CDCl_3$) 19.7 (Me_3C), 27.2 (Me_3C), 52.3 (O*Me*), 65.5 (C-1″), 78.1 (C-4/C-5), 83.8 (*C*Ph$_2$OMe), ~118 (br, C-1′), 127.7 (Ar), 127.9 (Ar), 128.0 (Ar), 128.2 (Ar), 128.7 (Ar), 128.9 (Ar), 129.9 (Ar), 130.0 (Ar), 134.0 (Ar), 135.8 (Ar), 141.5 (Ar), 141.9 (Ar), 151.4 (C-2′); *m*/*z* (EI) 758 (0.3%), 726 (10) and 197 (100). The NMR spectra indicated that the sample was a mixture of the title compound containing minor amounts (<10%) of boronic ester **13**. Separation was not possible at this stage; the structure of compound **13** was indirectly elucidated by isolating the corresponding cyclopropanation product.

(4*R*,5*R*)-2-[(*E*)-2-(Benzyloxymethyl)ethenyl]-4,5-bis[methoxydiphenylmethyl]-1,3,2-dioxaborolane (5c). Yield 47% (route 2), white foam; softening range = 65–72 °C; $[a]_D$ −46.1 (*c* 0.90 in $CHCl_3$) (Found: C, 78.44; H, 6.45. $C_{40}H_{39}BO_5$ requires C, 78.69; H, 6.44%); IR (film)/cm^{-1} 3039, 3005, 1344 and 1061; NMR δ_H (500 MHz; $CDCl_3$) 2.92 (6 H, s, O*Me*), 3.86 (2 H, dd, *J* 4.8 and 1.5, 1″-H), 4.33 (2 H, s, Ph*CH*$_2$O), 5.27 (1 H, dt, *J* 18.1 and 1.5, 1′-H), 5.28 (2 H, s, 4-H and 5-H), 6.17 (1 H, dt, *J* 18.1 and 4.8, 2′-H), 7.17–7.53 (25 H, m, Ar*H*); δ_C (125 MHz; $CDCl_3$) 51.8 (O*Me*), 71.6 (C-1″), 71.9 (Ph*C*H$_2$O), 77.7 (C-4/C-5), 83.8 (*C*Ph$_2$OMe), ~119 (br, C-1′), 127.3 (Ar), 127.3 (Ar), 127.5 (Ar), 127.6 (Ar), 127.6 (Ar), 127.8 (Ar), 128.3 (Ar), 128.5 (Ar), 129.7 (Ar), 138.2 (Ar), 141.1 (Ar), 141.4 (Ar), 148.7 (C-2′); *m*/*z* (FAB + NaI) 633 (3%) [(M + Na)$^+$] and 197 (100).

(4*R*,5*R*)-4,5-Bis[methoxydiphenylmethyl]-2-[(*E*)-2-(methoxymethoxymethyl)ethenyl]-1,3,2-dioxaborolane (5d). Yield 38% (route 2), white foam; softening range = 52–59 °C; $[a]_D$ −54.9 (*c* 1.10 in $CHCl_3$) (Found: C, 74.52; H, 6.72. $C_{35}H_{37}BO_6$ requires C, 74.47; H, 6.66%); IR (film)/cm^{-1} 3059, 3024, 1348 and 1077; NMR δ_H (500 MHz; $CDCl_3$) 2.92 (6 H, s, O*Me*), 3.23 (3 H, s, CH$_2$O*Me*), 3.90 (2 H, complex m, 1″-H), 4.46 (2 H, s, *CH*$_2$-OMe), 5.24 (1 H, dt, *J* 18.1 and 1.8, 1′-H), 5.27 (2 H, s, 4-H and 5-H), 6.13 (1 H, dt, *J* 18.1 and 4.7, 2′-H), 7.18–7.28 (20 H, m, Ar*H*); δ_C (125 MHz; $CDCl_3$) 51.8 (O*Me*), 55.2 (CH$_2$O*Me*), 68.4 (C-1″), 77.7 (C-4/C-5), 83.3 (*C*Ph$_2$OMe), 95.5 (*CH*$_2$OMe), ~118.5 (br, C-1′), 127.2 (Ar), 127.3 (Ar), 127.5 (Ar), 127.8 (Ar), 128.5 (Ar), 129.7 (Ar), 141.1 (Ar), 141.4 (Ar), 148.2 (C-2′); *m*/*z* (EI) 528 (0.1%), 519 (0.1) and 197 (100).

(4*R*,5*R*)-2-[(*E*)-2-(Benzoyloxymethyl)ethenyl]-4,5-bis[methoxydiphenylmethyl]-1,3,2-dioxaborolane (5e). Yield 60% (route 2), white foam; softening range = 71–76 °C; $[a]_D$ −47.3 (*c* 1.50 in $CHCl_3$) (Found: C, 76.72; H, 6.09. $C_{40}H_{37}BO_6$ requires C, 76.93; H, 5.97%); IR (film)/cm^{-1} 3059, 3031, 1723, 1348 and 1076; NMR δ_H (500 MHz; $CDCl_3$) 2.96 (6 H, s, O*Me*), 4.72 (2 H, dd, *J* 4.5 and 1.6, 1″-H), 5.36 (2 H, s, 4-H and 5-H), 5.40 (1 H, dt, *J* 18.1 and 1.6, 1′-H), 6.29 (1 H, dt, *J* 18.1 and 4.5, 2′-H), 7.25–7.36 (20 H, m, Ar*H*), 7.41–7.44 (2 H, m, Ar*H*), 7.53–7.56 (1 H, m, Ar*H*), 8.01–8.03 (2 H, m, Ar*H*); δ_C (125 MHz; $CDCl_3$) 51.8 (O*Me*), 65.6 (C-1″), 77.7 (C-4/C-5), 83.3 (*C*Ph$_2$OMe), ~119 (br, C-1′), 127.3 (Ar), 127.3 (Ar), 127.5 (Ar), 127.8 (Ar), 128.3 (Ar), 128.4 (Ar), 129.6 (Ar), 129.7 (Ar), 130.0 (Ar), 133.0 (Ar), 141.0 (Ar), 141.3 (Ar), 145.4 (C-2′), 165.9 (C=O); *m*/*z* (EI) 624 (<0.3%) and 197 (100).

(4*R*,5*R*)-4,5-Bis(methoxydiphenylmethyl)-2-cyclohexyl-1,3,2-dioxaborolane (9). White foam; softening range = 95–100 °C; $[a]_D$ −120 (*c* 1.30 in $CHCl_3$) (Found: C, 78.98; H, 7.30. $C_{36}H_{39}BO_4$ requires C, 79.12; H, 7.19%); IR (film)/cm^{-1} 3059, 2924, 1336 and 1076; NMR δ_H (500 MHz; $CDCl_3$) 0.33 (1 H, tt, *J* 12.3 and 3.3, 1′-H), 0.68–1.47 (10 H, m, -*CH*$_2$-), 2.93 (6 H, s, O*Me*), 5.18 (2 H, s, 4-H and 5-H), 7.18–7.28 (20 H, m, Ar*H*); δ_C (125 MHz; $CDCl_3$) 22.7 (C-1′), 27.1 (-*CH*$_2$-), 27.7 (-*CH*$_2$-), 27.8 (-*CH*$_2$-), 27.9 (-*CH*$_2$-), 28.2 (-*CH*$_2$-), 52.1 (O*Me*), 83.8 (*C*Ph$_2$OMe), 127.5 (Ar), 127.6 (Ar), 127.8 (Ar), 128.1 (Ar), 128.9 (Ar), 130.2 (Ar), 141.8 (Ar), 141.9 (Ar); *m*/*z* (EI) 514 (1%) and 197 (100).

Cyclopropanation of alkenylboronic esters

General procedure C (method A). The alkenylboronic ester (1 equiv.) was dissolved in diethyl ether (1 mL per mmol boronic ester) and 5 mol% palladium(II) acetate added. The suspension was treated for 2 min in an ultrasonic bath. After cooling the mixture to 0 °C, diazomethane[50–52] (25 mL per mmol boronic ester of an approx. 0.5 M solution in diethyl ether) was slowly (1 mL min^{-1}) added by means of a syringe-pump.[53] Unreacted diazomethane was destroyed by stirring the reaction mixture vigorously. Filtration through Celite, evaporation of the solvent under reduced pressure, followed by chromatographic purification led to analytically pure cyclopropylboronic esters. The diastereomeric ratios and yields are

given in Scheme 2; the reaction was typically performed on a 0.3–3 mmol scale.

General procedure D (method B). The alkenylboronic ester (1.0 equiv.) in dichloromethane (1 mL per mmol boronic ester) was added to a pre-formed cyclopropanating reagent [5.0 equiv. diiodomethane dissolved in dichloromethane (10 mL per mmol boronic ester), treated with diethylzinc solution (2.5 equiv. of a 1 M solution in hexane) at 0 °C]. Stirring was continued for 12 h at room temperature. After quenching the reaction with saturated aqueous ammonium chloride, the aqueous layer was extracted with dichloromethane (3×). The combined organic layer was dried over magnesium sulfate and the solvents removed under reduced pressure. The crude product was purified by flash-column chromatography; the reaction was typically performed on a 0.3–6 mmol scale.

(4*R*,5*R*,1′*S*,2′*S*)-2-[2-{*tert*-Butyl(diphenyl)siloxymethyl}-cyclopropyl]-4,5-bis[methoxydiphenylmethyl]-1,3,2-dioxaborolane (10b), (4*R*,5*R*,1′*R*,2′*R*)-2-[2-{*tert*-butyl(diphenyl)siloxymethyl}cyclopropyl]-4,5-bis[methoxydiphenylmethyl]-1,3,2-dioxaborolane (11b), and (4*R*,5*R*)-2-[1-{*tert*-butyl(diphenyl)-siloxymethyl}cyclopropyl]-4,5-bis(methoxydiphenylmethyl)-1,3,2-dioxaborolane (12). Yield 90% (general procedure C), white foam (Found: C, 77.39; H, 7.26. $C_{50}H_{53}BO_5Si$ requires C, 77.70; H, 6.91%); IR (film)/cm^{-1} 2931, 2856, 2360, 1388 and 1076; *m*/*z* (EI) 772 (0.1%), 740 (0.1) and 197 (100). The diastereoisomers **10b** and **11b**, and the regioisomer **12** were separated by means of MPLC (0.3% ethyl acetate in petroleum ether).

Major diastereoisomer **10b** (second eluted): softening range = 69–71 °C; $[\alpha]_D$ −26.7 (*c* 0.60 in $CHCl_3$); NMR δ_H (500 MHz; $CDCl_3$) −0.66 (1 H, ddd, *J* 9.5, 6.4, and 5.4 Hz, 1′-H), 0.28 (1 H, ddd, *J* 9.5, 5.3, and 3.3 Hz, 3′-H_{cis}), 0.33 (1 H, ddd, *J* 7.7, 6.5, and 3.3 Hz, 1 H, 3′-H_{trans}), 0.59 (1 H, complex m, 2′-H), 0.91 (9 H, s, Me_3C), 2.91 (6 H, s, O*Me*), 3.16 (1 H, dd, *J* 10.5 and 6.2, 1″-H_a), 3.54 (1 H, dd, *J* 10.5 and 4.6, 1″-H_b), 5.17 (2 H, s, 4-H and 5-H), 7.16–7.55 (30 H, m, Ar*H*); δ_C (125 MHz; $CDCl_3$) −3 (br, C-1′), 9.5 (C-3′), 19.6 (Me_3C), 20.2 (C-2′), 27.2 (Me_3C), 52.2 (O*Me*), 67.3 (C-1″), 78.0 (C-4/C-5), 83.7 (*C*Ph_2OMe), 127.6 (Ar), 127.6 (Ar), 127.8 (Ar), 127.9 (Ar), 128.0 (Ar), 128.2 (Ar), 128.8 (Ar), 129.9 (Ar), 130.0 (Ar), 134.3 (Ar), 136.0 (Ar), 141.6 (Ar), 141.8 (Ar).

Minor diastereoisomer **11b** (third eluted): softening range = 67–70 °C; $[\alpha]_D$ −77.7 (*c* 1.20 in $CHCl_3$); NMR δ_H (500 MHz; $CDCl_3$) −0.75 (1 H, ddd, *J* 9.9, 5.8, and 5.6 Hz, 1′-H), −0.01 (1 H, ddd, *J* 7.7, 6.0, and 3.4 Hz, 1 H, 3′-H_{trans}), 0.20 (1 H, ddd, *J* 9.9, 5.2, and 3.4 Hz, 3′-H_{cis}), 0.81 (1 H, complex m, 2′-H), 0.93 (9 H, s, Me_3C), 2.93 (6 H, s, O*Me*), 3.05 (1 H, dd, *J* 10.7 and 7.2, 1″-H_a), 3.53 (1 H, dd, *J* 10.7 and 4.8, 1″-H_b), 5.17 (2 H, s, 4-H and 5-H), 7.16–7.54 (30 H, m, Ar*H*); δ_C (125 MHz; $CDCl_3$) −3 (br, C-1′), 10.1 (C-3′), 19.6 (Me_3C), 20.4 (C-2′), 27.3 (Me_3C), 52.1 (O*Me*), 68.2 (C-1″), 77.9 (C-4/C-5), 83.7 (*C*Ph_2OMe), 127.5 (Ar), 127.6 (Ar), 127.8 (Ar), 127.9 (Ar), 128.2 (Ar), 128.8 (Ar), 128.9 (Ar), 129.9 (Ar), 130.1 (Ar), 134.3 (Ar), 136.0 (Ar), 141.6 (Ar), 141.8 (Ar).

Regioisomer **12** (first eluted): colourless oil; $[\alpha]_D$ −55.5 (*c* 0.70 in $CHCl_3$); NMR δ_H (500 MHz; $CDCl_3$) −0.14 (1 H, ddd, *J* 8.9, 5.8, and 2.8 Hz, cyclopropyl-H_a), 0.24 (1 H, ddd, *J* 8.9, 5.8, and 2.8 Hz, cyclopropyl-H_b), 0.29 (1 H, ddd, *J* 8.9, 5.8, and 3.2 Hz, cyclopropyl-H_c), 0.34 (1 H, ddd, *J* 8.9, 5.8, and 3.2 Hz, cyclopropyl-H_d), 0.80 (9 H, s, Me_3C), 2.91 (6 H, s, O*Me*), 3.09 (1 H, d, *J* 10.1, 1″-H_a), 3.13 (1 H, d, *J* 10.1, 1″-H_b), 5.19 (2 H, s, 4-H and 5-H), 7.14–7.49 (30 H, m, Ar*H*); δ_C (125 MHz; $CDCl_3$) −9.5 (br, C-1′), 9.7 (C-2′), 18.3 (Me_3C), 19.6 (C-3′), 27.2 (Me_3C), 52.2 (O*Me*), 66.9 (C-1″), 78.1 (C-4/C-5), 83.8 (*C*Ph_2OMe), 127.6 (Ar), 127.7 (Ar), 127.8 (Ar), 127.9 (Ar), 128.2 (Ar), 128.8 (Ar), 129.7 (Ar), 130.2 (Ar), 136.0 (Ar), 136.1 (Ar), 141.8 (Ar), 142.0 (Ar).

(4*R*,5*R*,1′*S*,2′*S*)-2-[2-(Benzyloxymethyl)cyclopropyl]-4,5-bis-[methoxydiphenylmethyl]-1,3,2-dioxaborolane (10c) and (4*R*,5*R*,1′*R*,2′*R*)-2-[2-(benzyloxymethyl)cyclopropyl]-4,5-bis[methoxydiphenylmethyl]-1,3,2-dioxaborolane (11c). Yield 88% (general procedure C), white foam (Found: C, 78.49; H, 6.75. $C_{41}H_{41}BO_5$ requires C, 78.84; H, 6.62%); IR (film)/cm^{-1} 3039, 3002, 1352 and 1061; *m*/*z* (FAB + NaI) 647 (0.1%) [(M + Na)$^+$] and 197 (100). The diastereoisomers **10c** and **11c** were separated by means of MPLC (2% ethyl acetate in petroleum ether).

Major diastereoisomer **10c** (second eluted): softening range = 68–71 °C; $[\alpha]_D$ −48.5 (*c* 1.00 in $CHCl_3$); NMR δ_H (500 MHz; $CDCl_3$) −0.69 (1 H, ddd, *J* 9.5, 6.3, and 5.3 Hz, 1′-H), 0.29 (1 H, ddd, *J* 9.5, 5.2, and 3.5 Hz, 3′-H_{cis}), 0.46 (1 H, ddd, *J* 8.4, 6.3, and 3.5 Hz, 3′-H_{trans}), 0.64 (1 H, ddddd, *J* 8.4, 7.8, 5.3, 5.2 and 5.2 Hz, 2′-H), 2.85 (1 H, dd, *J* 10.2 and 7.8, 1″-H_a), 2.95 (6 H, s, O*Me*), 3.38 (1 H, dd, *J* 10.2 and 5.2, 1″-H_b), 4.37 (1 H, d, *J* 12.1, PhCH_aH_bO), 4.43 (1 H, d, *J* 12.1, PhCH_aH_bO), 5.21 (2 H, s, 4-H and 5-H), 7.18–7.31 (25 H, m, Ar*H*); δ_C (125 MHz; $CDCl_3$) −3 (br, C-1′), 10.1 (C-3′), 17.4 (C-2′), 51.7 (O*Me*), 72.3 (PhCH_2O), 74.6 (C-1″), 77.5 (C-4/C-5), 83.2 (*C*Ph_2OMe), 127.2 (Ar), 127.4 (Ar), 127.5 (Ar), 127.5 (Ar), 127.7 (Ar), 127.9 (Ar), 128.3 (Ar), 128.3 (Ar), 129.7 (Ar), 138.6 (Ar), 141.2 (Ar), 141.3 (Ar).

Minor diastereoisomer **11c** (first eluted): softening range = 79–83 °C; $[\alpha]_D$ −89.0 (*c* 0.60 in $CHCl_3$); NMR δ_H (500 MHz; $CDCl_3$) −0.69 (1 H, ddd, *J* 9.9, 6.2, and 5.4 Hz, 1′-H), 0.10 (1 H, ddd, *J* 8.5, 6.2, and 3.5 Hz, 3′-H_{trans}), 0.23 (1 H, ddd, *J* 9.9, 5.2, and 3.5 Hz, 3′-H_{cis}), 1.00 (1 H, ddddd, *J* 8.5, 7.6, 5.4, 5.2 and 5.2 Hz, 2′-H), 2.92 (1 H, dd, *J* 10.2 and 7.6, 1″-H_a), 2.95 (6 H, s, O*Me*), 3.27 (1 H, dd, *J* 10.2 and 5.2, 1″-H_b), 4.35 (1 H, d, *J* 12.0, PhCH_aH_bO), 4.38 (1 H, d, *J* 12.0, PhCH_aH_bO), 5.21 (2 H, s, 4-H and 5-H), 7.17–7.39 (25 H, m, Ar*H*); δ_C (125 MHz; $CDCl_3$) −2 (br, C-1′), 10.1 (C-3′), 17.7 (C-2′), 51.7 (O*Me*), 72.4 (PhCH_2O), 74.8 (C-1″), 77.5 (C-4/C-5), 83.3 (*C*Ph_2OMe), 127.2 (Ar), 127.3 (Ar), 127.4 (Ar), 127.5 (Ar), 127.6 (Ar), 127.8 (Ar), 128.3 (Ar), 128.4 (Ar), 129.7 (Ar), 138.5 (Ar), 141.2 (Ar), 141.3 (Ar).

(4*R*,5*R*,1′*S*,2′*S*)-4,5-Bis[methoxydiphenylmethyl]-2-[2-{methoxymethoxymethyl}cyclopropyl]-1,3,2-dioxaborolane (10d) and (4*R*,5*R*,1′*R*,2′*R*)-4,5-bis[methoxydiphenylmethyl]-2-[2-{methoxymethoxymethyl}cyclopropyl]-1,3,2-dioxaborolane (11d). Yield 98% (general procedure C), white foam (Found: C, 74.60; H, 6.90. $C_{36}H_{39}BO_6$ requires C, 74.74; H, 6.80%); IR (film)/cm^{-1} 3058, 2983, 1386 and 1076; *m*/*z* (EI) 578 (0.1%), 546 (1) and 197 (100). Only the major diastereoisomers **10d** could be separated by means of MPLC (2% ethyl acetate in petroleum ether) and fully characterized; the NMR data of boronic ester **11d** (in Table 1) were obtained from the mixture.

Major diastereoisomer **10d** (second eluted): softening range = 100–102 °C; $[\alpha]_D$ −52.8 (*c* 1.00 in $CHCl_3$); NMR δ_H (500 MHz; $CDCl_3$) −0.64 (1 H, ddd, *J* 9.5, 6.3, and 5.3 Hz, 1′-H), 0.34 (1 H, ddd, *J* 9.5, 5.2, and 3.5 Hz, 3′-H_{cis}), 0.50 (1 H, ddd, *J* 8.5, 6.3, and 3.5 Hz, 3′-H_{trans}), 0.66 (1 H, ddddd, *J* 8.5, 7.9, 5.3, 5.3 and 5.2 Hz, 2′-H), 2.95 (1 H, dd, *J* 10.4 and 7.9, 1″-H_a), 3.00 (6 H, s, O*Me*), 3.31 (3 H, s, CH_2OMe), 3.46 (1 H, dd, *J* 10.4 and 5.3, 1″-H_b), 4.55 (2 H, complex m, CH_2OMe), 5.26 (2 H, s, 4-H and 5-H), 7.24–7.35 (20 H, m, Ar*H*); δ_C (125 MHz; $CDCl_3$) −2 (br, C-1′), 10.0 (C-3′), 17.5 (C-2′), 51.7 (O*Me*), 55.0 (CH_2OMe), 71.8 (C-1″), 77.5 (C-4/C-5), 83.3 (*C*Ph_2OMe), 95.7 (CH_2OMe), 127.5 (Ar), 127.6 (Ar), 127.8 (Ar), 128.0 (Ar), 128.4 (Ar), 129.7 (Ar), 141.2 (Ar), 141.3 (Ar).

(4*R*,5*R*,1′*S*,2′*S*)-2-[2-(Benzoyloxymethyl)cyclopropyl]-4,5-bis[methoxydiphenylmethyl]-1,3,2-dioxaborolane (10e) and (4*R*,5*R*,1′*R*,2′*R*)-2-[2-(benzoyloxymethyl)cyclopropyl]-4,5-bis[methoxydiphenylmethyl]-1,3,2-dioxaborolane (11e). Yield 96% (general procedure C), white foam (Found: C, 76.95; H, 6.31. $C_{41}H_{39}BO_6$ requires C, 77.12; H, 6.16%); IR (film)/cm^{-1} 3039,

3005, 1358 and 1060; *m/z* (FAB + NaI) 661 (47%) [(M + Na)$^+$] and 197 (100). The diastereoisomers **10e** and **11e** could not be separated by means of MPLC. The following data were obtained from the mixture.

Major diastereoisomer **10e**: NMR δ_H (500 MHz; $CDCl_3$) −0.62 (1 H, ddd, *J* 9.6, 6.4, and 5.3 Hz, 1′-H), 0.28 (1 H, ddd, *J* 9.6, 5.1, and 3.7 Hz, 3′-H_{cis}), 0.38 (1 H, ddd, *J* 8.2, 6.4, and 3.7 Hz, 3′-H_{trans}), 0.68 (1 H, ddddd, *J* 8.2, 7.6, 6.1, 5.3 and 5.1 Hz, 2′-H), 2.81 (6 H, s, O*Me*), 3.71 (1 H, dd, *J* 11.4 and 7.6, 1″-H_a), 3.94 (1 H, dd, *J* 11.4 and 6.1, 1″-H_b), 5.10 (2 H, s, 4-H and 5-H), 7.17–7.39 (25 H, m, Ar*H*); δ_C (125 MHz; $CDCl_3$) −2 (br, C-1′), 9.9 (C-3′), 16.4 (C-2′), 51.7 (O*Me*), 69.3 (C-1″), 77.6 (C-4/C-5), 83.3 (*C*Ph_2OMe), 127.2 (Ar), 127.3 (Ar), 127.5 (Ar), 127.6 (Ar), 127.8 (Ar), 128.3 (Ar), 128.4 (Ar), 129.5 (Ar), 129.7 (Ar), 132.5 (Ar), 141.2 (Ar), 141.3 (Ar), 166.5 (C=O).

Minor diastereoisomer **11e**: NMR δ_H (500 MHz; $CDCl_3$) −0.62 (1 H, ddd, *J* 10.0, 6.2, and 5.4 Hz, 1′-H), 0.00 (1 H, ddd, *J* 7.6, 6.3, and 3.7 Hz, 3′-H_{trans}), 0.22 (1 H, ddd, *J* 10.0, 5.1, and 3.7 Hz, 3′-H_{cis}), 1.00 (1 H, ddddd, *J* 7.6, 7.4, 6.6, 5.4 and 5.1 Hz, 2′-H), 2.81 (6 H, s, O*Me*), 3.75 (1 H, dd, *J* 11.4 and 7.4, 1″-H_a), 3.85 (1 H, dd, *J* 11.4 and 6.6, 1″-H_b), 5.10 (2 H, s, 4-H and 5-H), 7.17–7.39 (25 H, m, Ar*H*); δ_C (125 MHz; $CDCl_3$) −2 (br, C-1′), 10.0 (C-3′), 16.7 (C-2′), 51.7 (O*Me*), 69.3 (C-1″), 77.6 (C-4/C-5), 83.3 (*C*Ph_2OMe), 127.1 (Ar), 127.2 (Ar), 127.3 (Ar), 127.7 (Ar), 128.0 (Ar), 128.2 (Ar), 128.6 (Ar), 129.4 (Ar), 129.5 (Ar), 130.3 (Ar), 141.2 (Ar), 141.3 (Ar), 166.7 (C=O).

(*S*)-(−)-4-(2,2-Dibromoethenyl)-2,2-dimethyl-1,3-dioxolane (15)

By following the procedure as described by Jiang and Ma,[28] partially racemized product **15** was obtained. Yield 61%, bp 50 °C (0.35 torr); $[a]_D$ −2.6 [*c* 1.1 in MeOH; lit.[54] −3.6 (*c* 3.8 in MeOH)] (Found: C, 29.39; H, 3.51; Br, 55.74. $C_7H_{10}O_2Br$ requires C, 29.40; H, 3.52; Br, 55.88%); IR (film)/cm^{-1} 2980, 2936, 1370 and 1040; NMR δ_H (500 MHz; $CDCl_3$) 1.37 (3 H, s, *Me*), 1.41 (3 H, s, *Me*), 3.67 (1 H, dd, *J* 8.4 and 6.5 Hz, 5-H_a), 4.19 (1 H, dd, *J* 8.4 and 6.3 Hz, 5-H_b), 4.71 (1 H, ddd, *J* 7.6, 6.5 and 6.3 Hz, 4-H), 6.52 (1 H, d, *J* 7.6 Hz, 1′-H); δ_C (125 MHz; $CDCl_3$) 26.0 (*Me*), 27.9 (*Me*), 68.4 (C-5), 76.5 (C-4), 93.0 (C-1′), 110.4 (C-2), 137.5 (C-2′); *m/z* (EI) 284 (2%), 286 (4) and 288 (2).

(*S*)-(+)-4-Ethynyl-2,2-dimethyl-1,3-dioxolane (16)

By following the procedure as described by Jiang and Ma,[28] partially racemized product **16** was obtained. Yield 43%; $[a]_D$ 21.1 [*c* 1.10 in $CHCl_3$; lit.[54] 43.0 (*c* 1.00 in CCl_4) or lit.[28] 33.8 (*c* 1.00 in $CHCl_3$)].

A solution of aldehyde **14**[25–27] (1.03 g, 7.90 mmol) and the *Bestmann–Ohira* reagent **17**[30–35] (2.42 g, 12.6 mmol) in methanol (50 mL) was cooled to 0 °C. Potassium carbonate (2.33 g, 16.8 mmol) was gradually added (30 min). The mixture was stirred for 12 h, allowing it to warm to room temperature. Saturated aqueous ammonium chloride (50 mL) was added and the aqueous solution extracted with pentane (2 × 250 mL). The organic layer was separated, dried over magnesium sulfate, and the solvent carefully evaporated under reduced pressure. After purification by flash-column chromatography (eluent pentane–diethyl ether 10:1), alkyne **16** (700 mg, 5.50 mmol; 69%) was isolated as a colourless liquid, $[a]_D$ 40.6 (*c* 1.1 in $CHCl_3$) (Found: C, 66.12; H, 8.02. $C_7H_{10}O_2$ requires C, 66.65; H, 7.99%); IR (film)/cm^{-1} 3290, 2990, 2940, 2120, 1370 and 1065; NMR δ_H (500 MHz; $CDCl_3$) 1.35 (3 H, s, *Me*), 1.47 (3 H, s, *Me*), 2.47 (1 H, d, *J* 2.3 Hz, 2′-H), 3.92 (1 H, dd, *J* 8.1 and 6.2 Hz, 5-H_a), 4.14 (1 H, dd, *J* 8.1 and 6.4 Hz, 5-H_b), 4.67 (1 H, ddd, *J* 6.4, 6.2 and 2.3 Hz, 4-H); δ_C (125 MHz; $CDCl_3$) 26.3 (*Me*), 26.5 (*Me*), 65.6 (C-5), 70.2 (C-2′), 74.3 (C-4), 81.8 (C-1′), 110.9 (C-2); *m/z* (EI, AUTO -CI) 127.0754 [(M + H)$^+$. $C_7H_{11}O_2$ requires 127.0759]; 127 (20%) and 111 (100).

(4*R*,5*R*,4″*S*)-2-[(*E*)-2-(2,2-dimethyl-1,3-dioxolan-4-yl)ethenyl]-4,5-bis(methoxydiphenylmethyl)-1,3,2-dioxaborolane (18)

Following the general procedure A, the product **18** was isolated in 30% yield; general procedure B: yield 80% (route 2), white foam; softening range = 76–79 °C; $[a]_D$ −41.5 (*c* 1.40 in $CHCl_3$) (Found: C, 75.45; H, 6.80. $C_{37}H_{39}BO_6$ requires C, 75.26; H, 6.66%); IR (film)/cm^{-1} 3058, 2937, 1379 and 1075; NMR δ_H (500 MHz; $CDCl_3$) 1.27 (3 H, s, *Me*), 1.28 (3 H, s, *Me*), 2.92 (6 H, s, O*Me*), 3.38 (1 H, dd, *J* 8.1 and 7.4 Hz, 5″-H_a), 3.93 (1 H, dd, *J* 8.1 and 6.5 Hz, 5″-H_b), 4.30 (1 H, dddd, *J* 7.4, 6.5, 5.8 and 1.3 Hz, 4″-H), 5.25 (1 H, dd, *J* 18.1 and 1.3, 1′-H), 5.28 (2 H, s, 4-H and 5-H), 6.03 (1 H, dd, *J* 18.1 and 5.8, 2′-H), 7.16–7.36 (20 H, m, Ar*H*); δ_C (125 MHz; $CDCl_3$) 25.8 (*Me*), 26.5 (*Me*), 51.8 (O*Me*), 69.0 (C-5″), 77.6, 77.7 (C-4″ and C-4/C-5), 83.3 (*C*Ph_2OMe), 110.9 (C-2″), ~120 (br, C-1′), 127.3 (Ar), 127.3 (Ar), 127.5 (Ar), 127.8 (Ar), 128.4 (Ar), 129.7 (Ar), 141.0 (Ar), 141.3 (Ar), 149.2 (C-2′); *m/z* (EI) 590 (0.1%), 575 (2), 558 (2) and 197 (100).

(4*S*,5*S*,4″*S*)-2-[(*E*)-2-(2,2-Dimethyl-1,3-dioxolan-4-yl)ethenyl]-4,5-bis(methoxydiphenylmethyl)-1,3,2-dioxaborolane (19)

Following the general procedure A, the product **18** was isolated in 27% yield; general procedure B: yield 50% (route 2), white foam; softening range = 77–80 °C; $[a]_D$ +67.9 (*c* 1.10 in $CHCl_3$) (Found: C, 74.98; H, 6.87. $C_{37}H_{39}BO_6$ requires C, 75.26; H, 6.66%); IR (film)/cm^{-1} 3058, 2937, 1379 and 1075; NMR δ_H (500 MHz; $CDCl_3$) 1.34 (3 H, s, *Me*), 1.43 (3 H, s, *Me*), 2.97 (6 H, s, O*Me*), 3.42 (1 H, dd, *J* 8.1 and 7.4 Hz, 5″-H_a), 3.98 (1 H, dd, *J* 8.1 and 6.5 Hz, 5″-H_b), 4.37 (1 H, dddd, *J* 7.4, 6.5, 5.8 and 1.3 Hz, 4″-H), 5.32 (1 H, dd, *J* 18.1 and 1.3, 1′-H), 5.35 (2 H, s, 4-H and 5-H), 6.10 (1 H, dd, *J* 18.1 and 5.8, 2′-H), 7.24-7.37 (20 H, m, Ar*H*); δ_C (125 MHz; $CDCl_3$) 26.2 (*Me*), 26.9 (*Me*), 52.2 (O*Me*), 69.4 (C-5″), 78.0, 78.1 (C-4″ and C-4/C-5), 83.7 (*C*Ph_2OMe), 110.0 (C-2″), ~120 (br, C-1′), 127.7 (Ar), 127.7 (Ar), 127.9 (Ar), 128.2 (Ar), 128.8 (Ar), 130.1 (Ar), 141.4 (Ar), 141.7 (Ar), 149.6 (C-2′); *m/z* (EI) 590 (0.1%), 575 (2), 558 (2) and 197 (100).

(4*S*″)-2-[(*E*)-2-(2,2-Dimethyl-1,3-dioxolan-4-yl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (20)

Yield 56% (route 2, lit.[55] 90%), colourless solid: mp 35 °C; $[a]_D$ +35.2 (*c* 1.10 in $CHCl_3$) (Found: C, 61.47; H, 9.08. $C_{13}H_{23}BO_4$ requires C, 61.44; H, 9.12%); IR (film)/cm^{-1} 2982, 2935, 1372 and 1062; NMR δ_H (500 MHz; $CDCl_3$) 1.23 (6 H, s, *Me*), 1.24 (6 H, s, *Me*), 1.36 (3 H, s, *Me*), 1.40 (3 H, s, *Me*), 3.61 (1 H, dd, *J* 8.2 and 7.5 Hz, 5″-H_a), 4.08 (1 H, dd, *J* 8.2 and 6.4 Hz, 5″-H_b), 4.37 (1 H, dddd, *J* 7.5, 6.4, 6.4 and 1.2 Hz, 4″-H), 5.64 (1 H, dd, *J* 18.0 and 1.2, 1′-H), 6.52 (1 H, dd, *J* 18.0 and 6.4, 2′-H); δ_C (125 MHz; $CDCl_3$) 24.7 (2 × *Me*), 24.8 (2 × *Me*), 25.9 (*Me*), 26.5 (*Me*), 69.0 (C-5″), 78.0 (C-4″), 83.4 (2 × Me_2CO), 109.6 (C-2″), ~121 (br, C-1′), 149.5 (C-2′); *m/z* (EI) 253 (21%), 197 (49) and 101 (100).

(4*R*,5*R*,1′*S*,2′*S*,4″*S*)-2-[2-(2,2-Dimethyl-1,3-dioxolan-4-yl)-cyclopropyl]-4,5-bis(methoxydiphenylmethyl)-1,3,2-dioxaborolane (21) and (4*R*,5*R*,1′*R*,2′*R*,4″*S*)-2-[2-(2,2-dimethyl-1,3-dioxolan-4-yl)cyclopropyl]-4,5-bis(methoxydiphenylmethyl)-1,3,2-dioxaborolane (22)

Following the general procedure C, the product **21/22** was isolated in 93% yield as a 83:17 mixture; general procedure D: yield 58% (dr 11:89), white foam (Found: C, 75.59; H, 7.03. $C_{38}H_{41}BO_6$ requires C, 75.50; H, 6.84%); IR (film)/cm^{-1} 3058, 2937, 1369 and 1076; *m/z* (EI) 604.2996 [(M)$^+$. $C_{38}H_{41}BO_6$ requires 604.2996]; 604 (0.1%) and 197 (100). The diastereoisomers **21** and **22** were separated by means of MPLC (2% ethyl acetate in petroleum ether).

Compound **21** (first eluted): mp 142 °C; $[a]_D$ −35.1 (*c* 1.00 in $CHCl_3$); NMR δ_H (500 MHz; $CDCl_3$) −0.48 (1 H, ddd, *J* 9.6,

6.4, and 5.1 Hz, 1′-H), 0.24 (1 H, ddd, *J* 9.6, 5.2, and 3.6 Hz, 3′-H_{cis}), 0.35 (1 H, ddd, *J* 8.0, 6.4, and 3.6 Hz, 3′-H_{trans}), 0.55 (1 H, dddd, *J* 8.0, 7.4, 5.2 and 5.1 Hz, 2′-H), 1.21 (3 H, s, *Me*), 1.34 (3 H, s, *Me*), 2.92 (6 H, s, O*Me*), 3.32 (1 H, ddd, *J* 7.8, 7.4 and 6.0 Hz, 4″-H), 3.42 (1 H, dd, *J* 7.8 and 7.8 Hz, 5″-H_a), 3.86 (1 H, dd, *J* 7.8 and 6.0 Hz, 5″-H_b), 5.17 (2 H, s, 4-H and 5-H), 7.16–7.29 (20 H, m, Ar*H*); δ_C (125 MHz; $CDCl_3$) −2 (br, C-1′), 7.6 (C-3′), 19.4 (C-2′), 25.6 (*Me*), 26.8 (*Me*), 51.7 (O*Me*), 69.0 (C-5″), 77.7 (C-4/C-5), 80.0 (C-4″), 83.3 (*C*Ph_2OMe), 108.7 (C-2″), 127.1 (Ar), 127.4 (Ar), 127.5 (Ar), 127.7 (Ar), 128.3 (Ar), 129.7 (Ar), 141.2 (Ar), 141.4 (Ar).

Compound **22** (second eluted): mp 130 °C; $[a]_D$ −75.1 (*c* 1.10 in $CHCl_3$); NMR δ_H (500 MHz; $CDCl_3$) −0.68 (1 H, ddd, *J* 9.9, 6.1, and 5.5 Hz, 1′-H), 0.11 (1 H, ddd, *J* 7.5, 6.2, and 3.7 Hz, 3′-H_{trans}), 0.33 (1 H, ddd, *J* 9.9, 5.0, and 3.7 Hz, 3′-H_{cis}), 0.81 (1 H, dddd, *J* 8.4, 7.5, 5.5 and 5.0 Hz, 2′-H), 1.20 (3 H, s, *Me*), 1.30 (3 H, s, *Me*), 2.92 (6 H, s, O*Me*), 3.26 (1 H, ddd, *J* 8.4, 7.4 and 6.1 Hz, 4″-H), 3.63 (1 H, dd, *J* 7.8 and 7.8 Hz, 5″-H_a), 3.82 (1 H, dd, *J* 7.8 and 6.0 Hz, 5″-H_b), 5.20 (2 H, s, 4-H and 5-H), 7.19–7.25 (20 H, m, Ar*H*); δ_C (125 MHz; $CDCl_3$) −2 (br, C-1′), 9.8 (C-3′), 19.7 (C-2′), 25.6 (*Me*), 26.8 (*Me*), 51.7 (O*Me*), 69.2 (C-5″), 77.5 (C-4/C-5), 81.2 (C-4″), 83.3 (*C*Ph_2OMe), 108.9 (C-2″), 127.3 (Ar), 127.3 (Ar), 127.5 (Ar), 127.8 (Ar), 128.4 (Ar), 129.7 (Ar), 141.2 (Ar), 141.2 (Ar).

(4*S*,5*S*,1′*R*,2′*R*,4″*S*)-2-[2-(2,2-Dimethyl-1,3-dioxolan-4-yl)cyclopropyl]-4,5-bis(methoxydiphenylmethyl)-1,3,2-dioxaborolane (23) and (4*S*,5*S*,1′*S*,2′*S*,4″*S*)-2-[2-(2,2-dimethyl-1,3-dioxolan-4-yl)cyclopropyl]-4,5-bis(methoxydiphenylmethyl)-1,3,2-dioxaborolane (24)

Following the general procedure C, the product **23/24** was isolated in 95% yield as a 50:50 mixture; general procedure D: yield 72% (dr 94:6), white foam (Found: C, 75.18; H, 7.07. $C_{38}H_{41}BO_6$ requires C, 75.50; H, 6.84%); IR (film)/cm^{-1} 3058, 2937, 1370 and 1076; *m*/*z* (EI) 604.2996 [$(M)^+$. $C_{38}H_{41}BO_6$ requires 604.2996]; 604 (0.1%), 572 (0.1) and 197 (100). The diastereoisomers **23** and **24** were separated by means of MPLC (2% ethyl acetate in petroleum ether).

Compound **23** (second eluted): mp 120 °C; $[a]_D$ 40.0 (*c* 1.00 in $CHCl_3$); NMR δ_H (500 MHz; $CDCl_3$) −0.68 (1 H, ddd, *J* 9.8, 6.3, and 5.4 Hz, 1′-H), 0.40 (1 H, ddd, *J* 9.8, 5.0, and 3.6 Hz, 3′-H_{cis}), 0.48 (1 H, ddd, *J* 7.5, 6.3, and 3.6 Hz, 3′-H_{trans}), 0.59 (1 H, dddd, *J* 8.1, 7.5, 5.4 and 5.0 Hz, 2′-H), 1.21 (3 H, s, *Me*), 1.32 (3 H, s, *Me*), 2.92 (6 H, s, O*Me*), 3.16 (1 H, ddd, *J* 8.1, 7.2 and 6.1 Hz, 4″-H), 3.49 (1 H, dd, *J* 8.0 and 7.2 Hz, 5″-H_a), 3.86 (1 H, dd, *J* 8.0 and 6.1 Hz, 5″-H_b), 5.20 (2 H, s, 4-H and 5-H), 7.16–7.25 (20 H, m, Ar*H*); δ_C (125 MHz; $CDCl_3$) −4 (br, C-1′), 9.4 (C-3′), 19.5 (C-2′), 25.6 (*Me*), 26.8 (*Me*), 51.7 (O*Me*), 69.3 (C-5″), 77.6 (C-4/C-5), 80.9 (C-4″), 83.3 (*C*Ph_2OMe), 108.8 (C-2″), 127.3 (Ar), 127.3 (Ar), 127.5 (Ar), 127.8 (Ar), 128.4 (Ar), 129.7 (Ar), 141.3 (Ar), 141.3 (Ar).

Compound **24** (first eluted): mp 100–102 °C; $[a]_D$ 88.3 (*c* 1.00 in $CHCl_3$); NMR δ_H (500 MHz; $CDCl_3$) −0.51 (1 H, ddd, *J* 10.0, 6.2, and 5.6 Hz, 1′-H), −0.04 (1 H, ddd, *J* 8.0, 6.2, and 3.6 Hz, 3′-H_{trans}), 0.21 (1 H, ddd, *J* 10.0, 5.2, and 3.6 Hz, 3′-H_{cis}), 0.79 (1 H, complex m, 2′-H), 1.20 (3 H, s, *Me*), 1.25 (3 H, s, *Me*), 2.93 (6 H, s, O*Me*), 3.36–3.38 (2 H, m, 4″-H and 5″-H_a), 3.82–3.84 (1 H, m, 5″-H_b), 5.17 (2 H, s, 4-H and 5-H), 7.16–7.27 (20 H, m, Ar*H*); δ_C (125 MHz; $CDCl_3$) −2 (br, C-1′), 7.7 (C-3′), 19.9 (C-2′), 25.6 (*Me*), 26.7 (*Me*), 51.7 (O*Me*), 68.8 (C-5″), 77.5 (C-4/C-5), 79.5 (C-4″), 83.2 (*C*Ph_2OMe), 108.6 (C-2″), 127.2 (Ar), 127.4 (Ar), 127.5 (Ar), 127.7 (Ar), 128.3 (Ar), 129.7 (Ar), 141.2 (Ar), 141.3 (Ar).

(1′*R*,2′*R*,4″*S*)-2-[2-(2,2-Dimethyl-1,3-dioxolan-4-yl)cyclopropyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (25) and (1′*S*,2′*S*,4″*S*)-2-[2-(2,2-dimethyl-1,3-dioxolan-4-yl)cyclopropyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (26)

Following the general procedure C, the product **25/26** was isolated in 69% yield as a 60:40 mixture; general procedure D: yield 60% (dr 95:5), colourless oil. The diastereoisomers **25** and **26** could not be separated and fully purified; all data were obtained from the mixtures. IR (film)/cm^{-1} 2982, 2935, 1380 and 1067; *m*/*z* (EI, AUTO-CI) 269.1928 [$(M + H)^+$. $C_{14}H_{26}BO_4$ requires 269.1924]; 269 (25%) and 253 (100).

Compound **25**: NMR δ_H (500 MHz; $CDCl_3$) −0.28 (1 H, ddd, *J* 9.8, 6.3, and 5.4 Hz, 1′-H), 0.67 (1 H, ddd, *J* 9.8, 5.0, and 3.7 Hz, 3′-H_{cis}), 0.79 (1 H, ddd, *J* 7.6, 6.3, and 3.7 Hz, 3′-H_{trans}), 1.13 (1 H, complex m, 2′-H), 1.18 (12 H, br s, 4 × *Me*), 1.31 (3 H, s, *Me*), 1.41 (3 H, s, *Me*), 3.38 (1 H, dddd, *J* 8.4, 7.2, 6.1 and 1.2 Hz, 4″-H), 3.67 (1 H, dd, *J* 8.2 and 7.2 Hz, 5″-H_a), 4.03 (1 H, dd, *J* 8.2 and 6.1 Hz, 5″-H_b); δ_C (125 MHz; $CDCl_3$) −3.5 (br, C-1′), 9.2 (C-3′), 19.9 (C-2′), 24.6 (4 × *Me*), 25.7 (*Me*), 26.8 (*Me*), 69.6 (C-5″), 81.1 (C-4″), 83.1 (2 × Me_2CO), 109.0 (C-2″).

Compound **26**: NMR δ_H (500 MHz; $CDCl_3$) −0.02 (1 H, ddd, *J* 9.8, 6.3, and 5.1 Hz, 1′-H), 0.54 (1 H, ddd, *J* 9.8, 5.1, and 3.7 Hz, 3′-H_{cis}), 0.63 (1 H, ddd, *J* 8.0, 6.3, and 3.7 Hz, 3′-H_{trans}), 1.11–1.16 (1 H, m, 2′-H), 1.17 (6 H, s, 2 × *Me*), 1.18 (6 H, s, 2 × *Me*), 1.23 (3 H, s, *Me*), 1.38 (6 H, s, *Me*), 3.51 (1 H, ddd, *J* 7.5, 6.0 and 6.0 Hz, 4″-H), 3.64 (1 H, dd, *J* 8.0 and 7.5 Hz, 5″-H_a), 4.01 (1 H, dd, *J* 8.0 and 6.0 Hz, 5″-H_b); δ_C (125 MHz; $CDCl_3$) −1.5 (br, C-1′), 7.4 (C-3′), 19.5 (C-2′), 24.5 (4 × *Me*), 24.7 (*Me*), 25.8 (*Me*), 69.2 (C-5″), 80.3 (C-4″), 83.0 (2 × Me_2CO), 108.9 (C-2″).

(1′*R*,2′*R*,4″*S*)-[2-(2,2-dimethyl-1,3-dioxolan-4-yl)cyclopropyl]-methanol (27)

Cyclopropylboronic ester **25** (287 mg, 1.00 mmol) and chloroiodomethane (0.15 mL, 2.00 mmol) were dissolved in tetrahydrofuran and the solution cooled to −78 °C. Butyllithium (1.25 mL of a 1.6 M solution in hexane, 2.00 mmol) was slowly added, the reaction mixture warmed up to room temperature and stirred for 2 d. A 1:1 mixture of 30% hydrogen peroxide and 3 M aqueous sodium hydroxide (5 mL) was carefully added and stirring continued until TLC indicated complete consumption of the intermediate. Dilution with diethyl ether (10 mL) was followed by the addition of a saturated aqueous ammonium chloride solution (5 mL). After extraction of the aqueous layer, drying with magnesium sulfate and evaporation of the organic solvents under reduced pressure, the crude product was subjected to flash-column chromatography (petroleum ether–ethyl acetate 4:1 to 1:1). Yield 67% (dr >95:5), colourless oil. The spectroscopic data were in full agreement with published data.[42] $[a]_D$ −13 (*c* 1.7 in $CHCl_3$); IR (film)/cm^{-1} 3424, 2987, 1372 and 1064; *m*/*z* (EI, AUTO-CI) 173.1172 [$(M + 1)^+$. $C_9H_{16}O_3$ requires 173.1178]; 173 (15%) and 157 (100); NMR δ_H (500 MHz; $CDCl_3$) 0.53 (1 H, ddd, *J* 8.3, 5.1, and 5.0 Hz, 3′-H_{trans}), 0.60 (1 H, ddd, *J* 8.5, 5.1, and 5.0 Hz, 3′-H_{cis}), 0.84 (1 H, dddd, *J* 8.3, 7.8, 5.1, and 4.3 Hz, 2′-H), 0.99 (1 H, ddddd, *J* 8.5, 6.9, 6.8, 5.1, and 4.3 Hz, 1′-H), 1.27 (3 H, s, *Me*), 1.37 (3 H, s, *Me*), 1.79 (1 H, br s, OH), 3.40 (1 H, dd, *J* 11.2 and 6.9 Hz, 1-H_a), 3.46 (1 H, dd, *J* 11.2 and 6.8 Hz, 1-H_b), 3.57 (1 H, ddd, *J* 7.8, 7.2, and 5.9 Hz, 4″-H), 3.64 (1 H, dd, *J* 8.0 and 7.2 Hz, 5″-H_a), 4.04 (1 H, dd, *J* 8.0 and 5.9 Hz, 5″-H_b); δ_C (125 MHz; $CDCl_3$) 7.9 (C-3′), 17.8 (C-3′), 19.0, 19.1 (C-1′/C-2′), 25.6 (*Me*), 26.7 (*Me*), 65.8 (C-1), 69.1 (C-5″), 79.0 (C-4″), 108.02 (C-2″).

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